Standard Potentials of the (MO₂²⁺/MO₂⁺) and (M⁴⁺/M³⁺) Redox Systems for Neptunium and Plutonium.

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The formal potentials of the (MO_2^{2+}/MO_2^{+}) and (M^{4+}/M^{3+}) couples (where M = Np or Pu) were determined in CIO_4^- medium of varying ionic strength. These data have been determined by using the Bröngsted-Gugenheim-Scatchard specific ionic interaction theory to give the following standard potentials and interaction coefficients, $\Delta\epsilon = \epsilon(Ox,CIO_4^-) - \epsilon(Red,CIO_4^-)$, at 20°C:

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\begin{array}{lll} E^{\circ}(NpO_{2}^{\ 2+}/MO_{2}^{\ +}) &= 1.162 \pm 0.011 \ V/NHE & \Delta \epsilon = 0.21 \pm 0.03 \ kg/mole \\ E^{\circ}(PuO_{2}^{\ 2+}/PuO_{2}^{\ +}) &= 0.954 \pm 0.010 \ V/NHE & \Delta \epsilon = 0.29 \pm 0.03 \ kg/mole \\ E^{\circ}(Np^{4+}/Np^{3+}) &= 0.210 \pm 0.010 \ V/NHE & \Delta \epsilon = 0.33 \pm 0.03 \ kg/mole \\ E^{\circ}(Pu^{4+}/Pu^{3+}) &= 1.015 \pm 0.010 \ V/NHE & \Delta \epsilon = 0.54 \pm 0.03 \ kg/mole \\ \end{array}
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The published data on the neptunium and plutonium redox systems are reviewed, discussed and reinterpreted.